

This is a version of the following published document:

de Dios, M., González, Z., Romero, C., Gordo, B.,
Ferrari, B. (2016). Ti(C,N)-Fe/Ni/FeNi Core-Shell
Structures for Cermets Processing. *World PM2016
Proceedings*. EPMA, 2016. ISBN
978-1-899072-48-4

Manuscript refereed by Dr Ralph Useldinger (Ceratizit S.A., Luxembourg)

Ti(C,N)-Fe/Ni/FeNi Core-Shell Structures for Cermets Processing

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Abstract

This work proposes an alternative bottom-up approach to build cermet microstructures through the synthesis of metal hydroxide nanoparticles (NPs) on the surface of Ti(C,N) micrometric particles, creating core-shell Ti(C,N)-Ni(OH)₂ and Ti(C,N)-FeO(OH) and their subsequent calcination cycle. This calcination cycle will help us to obtain Ti(C,N)- based cermets with fine microstructure and low amount of metal binder avoiding mechanical milling, the risks of handling nanoparticles, as well as overcoming the lack of availability and the high prices of those metal nanoparticles. The obtained structures were characterized by differential thermal analysis (DTA), thermogravimetry (TG), X-Ray Diffraction (XRD) and field emission scanning electron microscopy (FE-SEM) and energy-dispersive X-Ray spectroscopy (EDX).

1.- Introduction

Compared to cemented carbides, Ti(C,N)-based cermets are gaining increasing technical importance [1,2], due to their excellent combination of hardness at high temperature, strength, wear resistance and thermal conductivity [3]. The production of those materials for metal cutting and rock drilling tools is a fast growing segment in industry [4]. Traditionally, in order to obtain a well-controlled microstructure, cermets are produced by ball milling during long time or mechano-chemical routes, leading to risks of contamination with the milling media [5,6]. However, the reduction in both, content and size of the binder phase, can be also achieved by bottom-up approaches, mainly profiting from the chemical routes such as electroless processes [7,8]. In this sense, the electroless plating method is inexpensive and widely used to modify the surface of many substrates; whatever was their electrical nature (nonconductors, semiconductors and metals).

Metal-coated ceramic powders refer to composite powders with a ceramic core and a metallic shell that can endow the ceramic powders with particular, electrical, magnetic and chemical properties. In this connection, electroless nickel/iron plating has been recognized as one of the most effective techniques for preparing metal-coated ceramics powders [9–11]. Recently, core-shell structures have been fabricated successfully in a number of materials with various methods, including self-assembly, the sonochemical method, vapor deposition polymerization, the seed-mediated growth technique and the chemical vapor-liquid reaction.

According to the needs for the desired properties, core-shell structures have been designed by the chemical precipitation of Ni/Fe nanoparticles (NPs) onto the surface of micrometric Ti(C,N) particles previously stabilized in an aqueous suspension. The electroless chemical precipitation of Ni²⁺ and Fe²⁺ salt were carried out for the preparation of fine nickel/iron NPs from the aqueous solution by precipitation with ammonium hydroxide.

Consequently a bottom-up route for obtaining Ti(C,N)/Ni/Fe/FeNi core-shell particles is proposed. This procedure consist of the electroless chemical precipitation of a nickel/iron salt to metallic NPs in aqueous solution, avoiding the use of any other kind of solvent resulting in an environmentally friendly route. Ni nitrate and Fe sulphate were used as salt precursors instead of the more common use of chlorides, sulfates and acetates, harmful precursors to the metal matrix.

Unlike what it has been commonly found in literature, the electroless chemical precipitation was modified in two main aspects. On the one hand, the typical sensitization and activation step used as pretreatment, adopted by many other investigators [12,13] has been replaced by a sonical activation. On the other hand, with this method it is going to be possible

reach higher solid volume contents (up to 30%) if it is compared with the traditional routes (up to 5%) [14,15].

2.- Experimental

2.1 Materials

The raw materials used were Nickel Nitrate Hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Iron Sulfate Heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and Potassium Hydroxide received from Panreac Company, Ammonium Hydroxide (NH_4OH) and Ammonium Citrate tribasic ($\text{HOC}(\text{CO}_2\text{NH}_4)(\text{CH}_2\text{CO}_2\text{NH}_4)$) were purchased from Sigma-Aldrich and Titanium Carbonitride with a mean size of 2.1 μm (Ti(C,N) powder Grade C) was received from H.C. Starck GmbH. The NPs precipitation was activated by the application of ultrasounds, using a US probe of 200 W (Sonopuls HD 2200, Bandelin electronic, Germany). The water used in this work was deionized water. All chemicals used in these experiments were of reagent grade and used without any further purification.

2.2 Homogeneous syntheses of nanoparticles

A typical preparation procedure is described as follow: a desired amount of metal salt precursor was dissolved into deionized water (**solution a**). Another mixture was obtained by dissolving ammonium citrate tribasic in an ammonium hydroxide solution (**mixture b**). Then, mixture b, was poured into **solution a** immediately with continued and vigorous ultrasonic power at controlled temperature, through the recirculation of a continuous flow of water from a cryothermal bath, all in a total solution volume of 50 mL. The overall reaction times were 90 minutes.

The variables involved in the synthesis are shown in Table 1.

Variable	Nickel route	Iron route
Salt precursor concentration	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1M)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (1M)
Salt Precursor - Ammonium hydroxide ratio	1:5	
Salt Precursor - Ammonium citrate ratio	120:1	
Temperature	50°C	
US time	90 min	
US power	50%	

Table 1 Summary of the formulation of the syntheses

2.3 Synthesis of Core-Shell Ti(C,N)-Ni and Ti(C,N)-Fe

In this case, core-shell structures have been obtained by the chemical precipitation of nickel hydroxide ($\text{Ni}(\text{OH})_2$) or iron oxy(hydroxide) ($\text{FeO}(\text{OH})$) NPs onto the surface of micrometric Ti(C,N) particles previously stabilized in the aqueous **solution a**. Then, a subsequent calcination step in a reducing atmosphere has been carried out in order to obtain the reduced metal Ni and Fe nanoparticles from the hydroxide and oxy(hydroxide) ones respectively.

2.4 Characterization of Ni nanoparticles and core-shell structures

Crystalline phase was characterized by X-ray diffraction (Siemens-Bruker D8 Advance, Germany) using Cu K α radiation ($\lambda=1.540598 \text{ \AA}$). The diffraction patterns were measured step by step (0.05° in 2θ).

Differential thermal analysis (DTA) and Thermogravimetric analysis (TG) were carried out in argon with constant heating rates of $10^\circ\text{C}/\text{min}$ up to temperatures of 800°C , in TG-DTA equipment (Perkin Elmer, USA).

Particle size and morphology were examined by field emission scanning electron microscopy (FE-SEM) in an S-4700 microscope (Hitachi, JAPAN) and EDX.

3.- Results

3.1.- Homogeneous syntheses of NPs

Fig. 1a shows the X-Ray Diffraction pattern of the Ni hydroxide powder synthesized. As it can be seen, this pattern with wider peaks is characteristic of a metastable turbostratic phase which corresponds to the α -Ni(OH)₂ polymorph (indexed using JCPDS card 22-0444). On the other hand, Fig. 1b shows the X-Ray Diffraction pattern of the amorphous FeO(OH) powder synthesized, mainly identified as α phase (Goethite) with a small amount of γ phase (Lepidocrocite) (indexed using JCPDS cards 29-0713 and 044-1415 respectively).

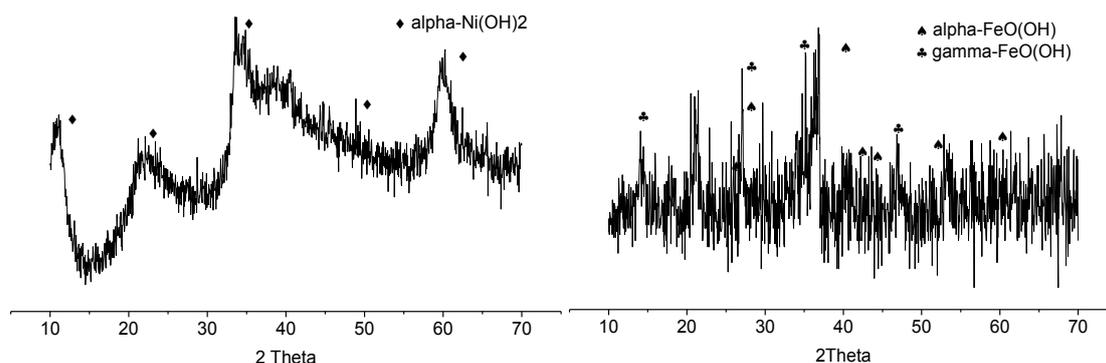


Fig. 1 XRD of synthesized powders (a) α -Ni(OH)₂ and (b) (α , γ)-FeO(OH)

In order to obtain the metallic phase from the composites designed, DTA-Tg analyzes (Fig. 2) were carried out to the homogeneous powders with the aim to obtain the adequate information for design an accurate calcination cycle.

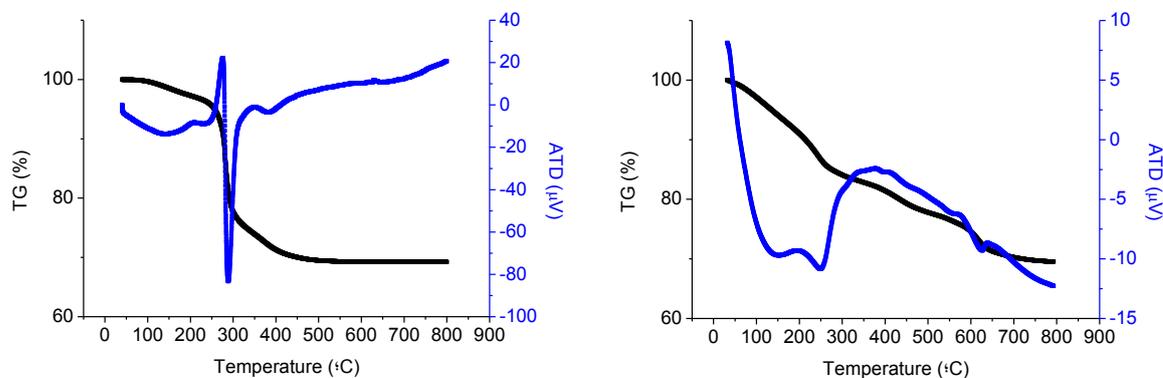


Fig. 2 DTA-Tg analyses of (a) α -Ni(OH)₂ and (b) (α , γ)-FeO(OH) synthesized powders

According to the information provided by these analyzes the calcination cycle will have the characteristics shown in Table 2.

Table 2. Calcination cycle characteristics

Final temperature	800°C
Heating/Cooling rate	10°C/min
Dwell time	30 min
Atmosphere	N ₂ /H ₂ (10%)

3.2.- Heterogeneous syntheses of Ti(C,N)-Ni and Ti(C,N)-Fe

Ti(C,N)-Ni and Ti(C,N)-Fe structures have been obtained by the chemical precipitation of Ni(OH)₂ and FeO(OH) NPs onto the surface of micrometric Ti(C,N) particles previously stabilized and their subsequent calcination cycle.

As it can be seen, in Fig. 3a shows the X-Ray Diffraction pattern of the Ti(C,N)-Ni core-shell particles. In this spectra appear the main reflections of the Ti(C,N) (36.6°, 42.5° and 61.4°) peaks corresponding to Miller indices (111), (200) and (220) according to the index card JCPDS n° 042-1488 and the two characteristic peaks of the face-centered cubic structure of Ni (45° and 52.4°), corresponding to Miller indices (111) and (200) respectively according to the index card JCPDS n° 04-0850 proving the obtaining core-shell particles.

On the other hand, Fig. 3b shows the X-Ray Diffraction pattern of the Ti(C,N)-Fe powder synthesized. The Ti(C,N) shows the same main reflections as in the previous case and Fe shows two characteristic peaks of its structure (44.6° and 65°), corresponding to Miller indices (110) and (200) (indexed using JCPDS card 06-0696).

Both patterns indicate the presence of oxide impurities (rutile and anatase phase) formed during the calcination cycle due to the high specific surface of the powders.

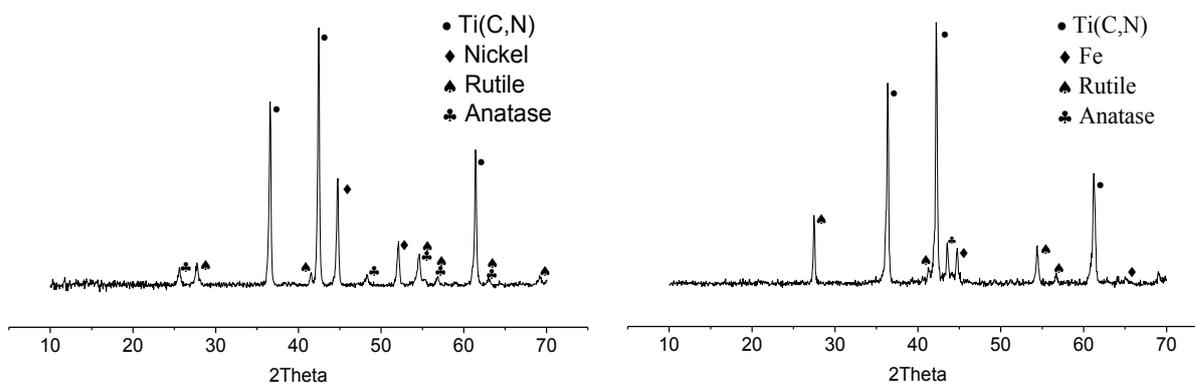


Fig 3 XRD of synthesized (a) Ti(C,N)-Ni and (b) Ti(C,N)-Fe core-shell particles

Fig. 4 shows FESEM micrographs of the resulting Ti(C,N)-Ni and Ti(C,N)-Fe core-shell structures obtained after the calcination step. The micrograph reveals brighter regions around the Ti(C,N) particles which correspond with a fine dispersion of Ni and Fe NPs which have grown onto the surface of those particles substrate. In a general inspection of the obtained structures of both syntheses, it can be concluded that the metallic shell have been formed.

Besides, elemental analyses of the composition (EDX) of the core-shell structures were done, which corroborate the attainment of the aforementioned structures. The composition obtained for both materials approach fairly well the ceramic/metal balance formulated as the starting composition (see Table 3).

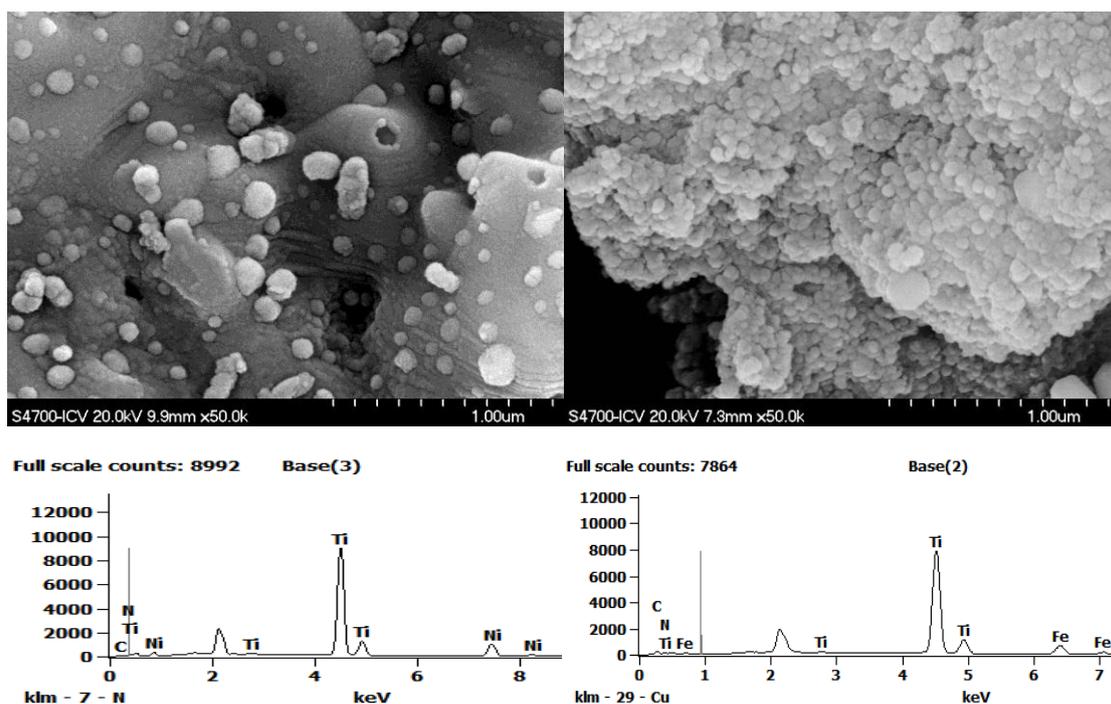


Fig 4 FESEM and EDX analyzes of synthesized (a and b) Ti(C,N)-Ni and (c and d) Ti(C,N)-Fe core-shell structures

Table 3 Expected vs obtained ceramic/metal balance for core-shell structures

Material	Theoretical composition	Obtained composition
Ti(C,N)-Ni	90/10 %vol	92/8 %vol
Ti(C,N)-Fe	90/10 %vol	94/6 %vol

4. Conclusions

- The synthesis of Ni(OH)₂ and FeO(OH) NP's by a precipitation method using ammonium hydroxide as precipitant agent in aqueous medium and its subsequent calcination cycle in order to obtain Ni and Fe NPs has been successfully achieved.
- Ti(C,N)-Ni and Ti(C,N)-Fe core-shells structures were obtained providing a route for the bottom up design of Ti(C,N)-FeNi interphases in cermets.
- With this method it is going to be possible to reach higher solid volume contents (up to 30%) if it is compared with the traditional routes (up to 5%).

Acknowledgements

The authors acknowledge the support of the projects S2013/MIT-2862, MAT2012-38650-C02-01, MAT2012-38650-C02-02 and MAT2015-70780-C4-1-P. M. Dios acknowledges MINECO through the grant BES-2013-065760 and Dr. Z Gonzalez acknowledges to MINECO through the grant PTQ-13-05985.

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